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EFFECT OF AQUEOUS CHLORINATION ON THE AROMATIC FRACTION OF DIESEL FUEL

ANALYSIS BY COMPUTER-ASSISTED GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

An investigation into the behaviour of aromatic hydrocarbons in chlorinated water is described. Aromatic fractions of diesel fuel were exposed to highly chlorinated water (100 mg/l free chlorine) for definite periods of time (1, 30 and 70 h), and the extracts were subjected to gas chromatographic–mass spectrometric analysis. Mass chromatograms of the various extracts, specific for aromatic hydrocarbons and possible chlorinated products, obtained by simple mathematical procedures, have been correlated with each other.

Conclusions are made on the reactivity of the various species: the rates of oxidation and chlorination are dependent on the number and orientation of the alkyl substituents. 1,3,5-Trimethylbenzene, a frequently encountered pollutant, shows a marked reactivity, its chlorination being almost complete after 1 h.

INTRODUCTION

Chlorine is widely used in water treatment as a disinfecting and oxidising agent[1]. In chlorination processes, organic constituents of water may be chlorinated to yield components which are of great concern in the consideration of water quality[2–4]. Details of the formation of various haloforms in chlorinated drinking waters have recently been published[5,6].

We have studied the possibility of chlorinated hydrocarbons originating from the chlorination of petroleum-derived compounds found in aqueous solutions. Such contamination of surface and drinking waters[7,8]. Substantial amounts of these materials are also normally present in domestic and industrial wastewater[9]. Petroleum hydrocarbons were chosen for this study because of their ubiquity and the bioresistant character of their chloro derivatives. Since aromatic hydrocarbons are more soluble in water and less resistant to chemical oxidation than aliphatic hydrocarbons[10], this study focuses on the aromatic fraction of diesel fuel.

Petroleum fractions are extremely complex mixtures which cannot be completely resolved into single components by high-resolution gas chromatography. We show that computer-assisted gas chromatography–mass spectrometry (GC–MS–COM) enables the specific detection of various groups of isomers and their chlorinated derivatives.

Chlorine disproportionates in water to produce hypochlorous and hydrochloric acids:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Under conditions normally prevailing at water treatment plants, the equilibrium position of this reaction is on the side of the acids, and only at a very low pH is a substantial amount of elemental chlorine present. Hypochlorous acid is a weak acid with a pK value of 7.5 at 20°. The reactions of organic compounds in chlorinated water are therefore dependent on both the chlorine concentration and the pH.

The aim of this study is to identify those components of diesel fuel (or the equivalent No. 2 fuel oil) which tend to form chlorinated hydrocarbons. This is achieved by specific fingerprints obtained by GC–MS–COM. We report correlations between precursors and chlorinated products, and discuss the results in the light of the reactivities and reaction pathways of the various compound types.

EXPERIMENTAL

100 μl of a commercial diesel fuel were fractionated on a silica column (11 × 1.0 cm, Kieselgel-40 (Merck Darmstadt, G.F.R.), activated at 275° for seven h). After eluting the aliphatic fraction with 30 ml of n-pentane, the aromatic constituents were obtained by elution with 30 ml of methylene chloride. The organic solvents had been carefully redistilled, and the water purified in a quartz distillation apparatus.

The methylene chloride fraction was concentrated at room temperature to 1 ml. A 300-μl aliquot of the solution was added to one litre of water which had been buffered with 100 ml of a 0.1 M phosphate buffer solution. By adding Javelle water (Bender and Hobein, Zürich, Switzerland) a concentration of 100 mg/l of free chlorine ($HOCl + {}^-OCl$) and a pH of 7.2 was attained. The chlorine concentration was determined by iodometric titration[11]. Samples of one litre each were allowed to react at room temperature for 1, 30 and 70 h, respectively. After chlorination the samples were extracted three times with 20 ml of n-pentane. The combined extracts were dried over sodium sulphate (Merck, puriss, heated at 750° for 24 h), and concentrated at room temperature to 300 μl. A second oil solution was prepared without adding any chlorine in order to analyze the starting material.

The GC–MS–COM investigations were performed on a Finnigan Model 1015 D apparatus in combination with a Finnigan Model 6000 Interactive Data System. The operation of the quadruple-type mass spectrometer was controlled by the computer, which acquired, stored, and processed the resulting data.

The gas chromatograph was equipped with a Grob-type injector[12] and a glass capillary column (OV-101, 50 m × 0.32 mm) which had been purchased from H. and G. Jaeggi, Trogen, Switzerland. The end of the glass capillary column was coupled to the mass spectrometer by means of a platinum capillary (0.1 mm I.D.) leading directly to the ion source. A piece of glass capillary tubing, 2 cm long, was melted on to one end of the platinum capillary so that it could be connected to the column with PTFE shrink tubing. By quenching the platinum tubing, elution conditions comparable to normal GC operation could be achieved. This interfacing technique has been described in detail by Neuner-Jehle and co-workers[13,14]. The MS operating conditions were: electron energy 70 eV, emission current 350 μA, preamplifier sensitivity 10^{-7} A/V.

3 μl of the concentrated extracts were injected without stream splitting onto the column at ambient temperature (approx. 28°). After 30 sec the split valve was opened, allowing the septum and injection port to be purged at a flow-rate of 15 ml/min[15]. Subsequent to the elution of the solvent, the oven temperature was programmed to 200° at 3°/min, and the temperature of the GC–MS interface oven was held at 180°. Helium at 30 p.s.i. was used as carrier gas.

Mass spectra were scanned continuously and stored on a magnetic disc. The initial parts of the chromatograms were recorded over a mass range from 33 to 199 atomic mass units (a.m.u.) with an integration time of 8 msec per a.m.u. For the second part, a mass range from 33 to 240 a.m.u. was recorded with 7 msec integration time per a.m.u. The cut between the two parts was set after the elution of acenaphthene, which could be monitored on the real time display.

The Data System 6000 enabled the data to be processed by a very rapid and convenient direct interaction with the computer. Mass spectra or reconstructed chromatograms could be stored in two different memory regions and could be added together or subtracted from each other as required. Negative values obtained by subtraction were set equal to zero. This operational facility is provided mainly for background subtraction of mass spectra, but it can also be used for combining reconstructed chromatograms.

Total ion current (TIC) chromatograms were established by adding together all ion currents of each spectrum and plotting them *versus* the spectrum numbers. Mass chromatograms (MC) were reconstructed selecting the specified ion or ion group and plotting the ion intensities in the same manner. These latter chromatograms indicate specifically those compounds which contain the selected elements in their mass spectra and structures, respectively[16]. For example, two compounds which have different retention times and can be detected specifically in a MC of the respective molecular masses, can be studied in one single chromatogram by adding together the two particular MC's.

RESULTS AND DISCUSSION

Initially, a control sample of the aromatic fraction of diesel fuel was studied without chlorination to provide background information on the complex mixture, and to test the detection techniques. Fig. 1 shows the TIC chromatograms resulting

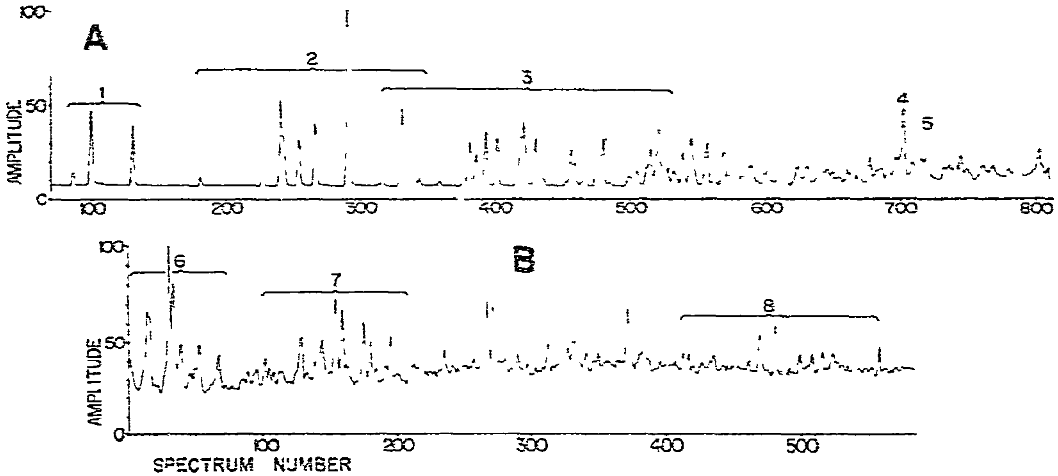

Fig 1. Reconstructed total ion current chromatogram of the aromatic fraction of diesel fuel. A, Mass range = 33–199 a.m.u ; integration time. 8 msec/a.m.u. B, Mass range = 33–244 a.m.u.; integration time: 7 msec/a.m.u. 1 = C_2-benzenes; 2 = C_3-benzenes; 3 = C_4-benzenes; 4 = 2-methylnaphtahlene; 5 = 1-methylnaphthalene, 6 = C_2-naphthalenes; 7 = C_3-naphthalenes; 8 = phenanthrene, anthracene, C_1-phenanthrenes/anthracenes.

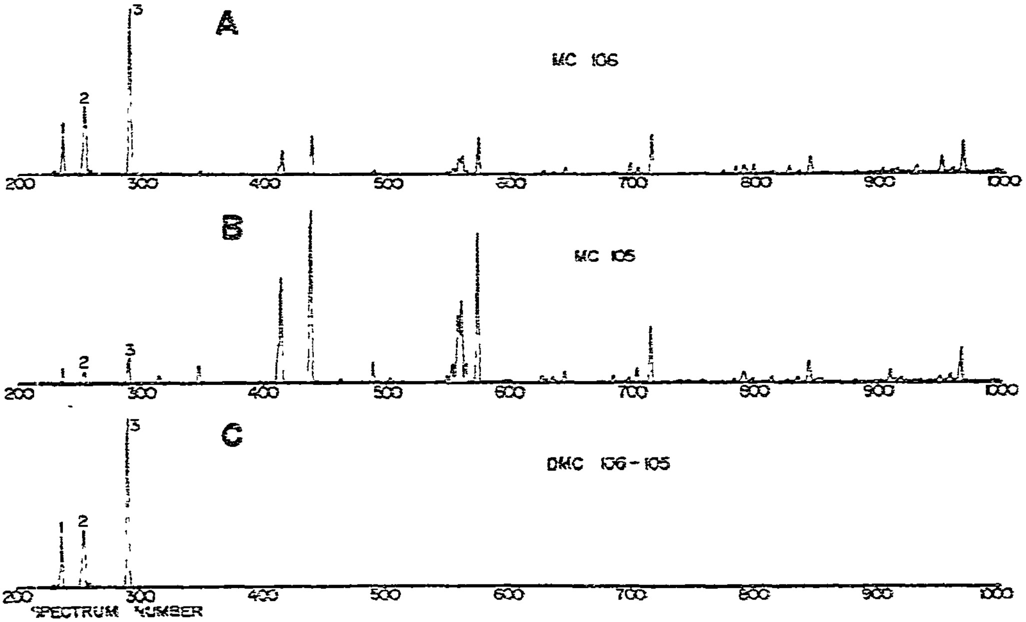

Fig. 2. Reconstructed mass chromatograms of the aromatic fraction of diesel fuel after 30 h chlorination. A = Mass chromatogram 106: B = mass chromatogram 105; C = difference mass chromatogram 106 − 105. 1 = Ethylbenzene; 2 = *m/p*-xylene; 3 = *o*-xylene.

from a GC–MS experiment. The chromatogram is split into two parts according to the storage in two different files of the disc memory. Because the highest peak of each part is used for normalization, the peak heights cannot be directly compared. The components in the second part are actually less abundant than the earlier eluting compounds. Most peaks contain more than one component, and many trace constituents are not detected. A large number of unresolved peaks gives rise to a chromatogram which cannot be reasonably interpreted. The ranges of the various compound types as indicated in Fig. 1 are based on MS evidence and on relative GC retention times.

The data resulting from the GC–MS experiment can be evaluated in a more sophisticated way using mass chromatographic techniques. Since most aromatic hydrocarbons show intense molecular ions in their mass spectra, they are well suited to specific detection by mass chromatography.

The mass chromatograms of several chlorinated mixtures were complicated; Fig. 2 exemplifies such a case and indicates how the disturbances can be removed. The MC for mass 106 (trace A) gives peaks for ethylbenzene, *o*/*m*-xylene (not resolved) and *p*-xylene. However, there are additional peaks which are eluted later than the C_2-benzenes*. The origin of this interference is demonstrated in trace B of Fig. 2, showing the MC for mass 105. In this chromatogram, the major peaks correspond to interference in trace A. This is due to the fact that compounds with ions of mass 105 have additional ions of mass 106 arising from the natural abundance of carbon-13 isotopes.

The selectivity is considerably improved by subtracting the MC for $M^+ - 1$ (MC 105, trace B) from the MC for M^+ (MC 106, trace A). In this way, only compounds having greater ion intensities of M^+ than of $M^+ - 1$ remain in the reconstructed chromatogram. Trace C of Fig. 2 demonstrates the efficiency of this subtraction procedure which eliminates the interfering peaks in the MC for the molecular ion of the C_2-benzenes.

In general, one can detect specifically a group of components which display in their mass spectra a greater intensity of ion A than ion B by subtracting MC (B^+) from MC (A^+). In this way all peaks which correspond to components having mass spectra with ion intensities $I(A^+) \leqslant I(B^+)$ are suppressed. If $I(A^+) > I(B^+)$, the difference mass chromatogram (DMC) reveals a peak with a height given by the intensity difference $I(A^+) - I(B^+)$. A similar technique was used to search for chlorinated hydrocarbons in the course of the impact of chlorine. The substitution by one or two chlorine atoms leads to an increase of the molecular mass by 34 or 68, respectively. The chlorinated products and their precursors could be represented in one single chromatogram by adding together the DMC for $[M^+ - (M^+ - 1)]$, $[(M^+ + 34) - (M^+ + 33)]$ and $[(M^+ + 68) - (M^+ + 67)]$. Figs. 3, 4 and 5 represent some of the resulting chromatograms for different types of compounds and varying reaction times.

Fig. 3 depicts the behaviour of C_3-benzenes. In the unchanged diesel fuel (reaction time 0, trace A), all eight possible isomeric C_3-benzenes were detected. Identification was based on their mass spectra and on co-injection gas chromatography of reference substances. Since acenaphthene (peak 16) also has a molecular mass of 154, this component also appears in the DMC (154 — 153). After a reaction time

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* C_n-benzene stands for benzenes with *n* additional aliphatic carbon atoms.

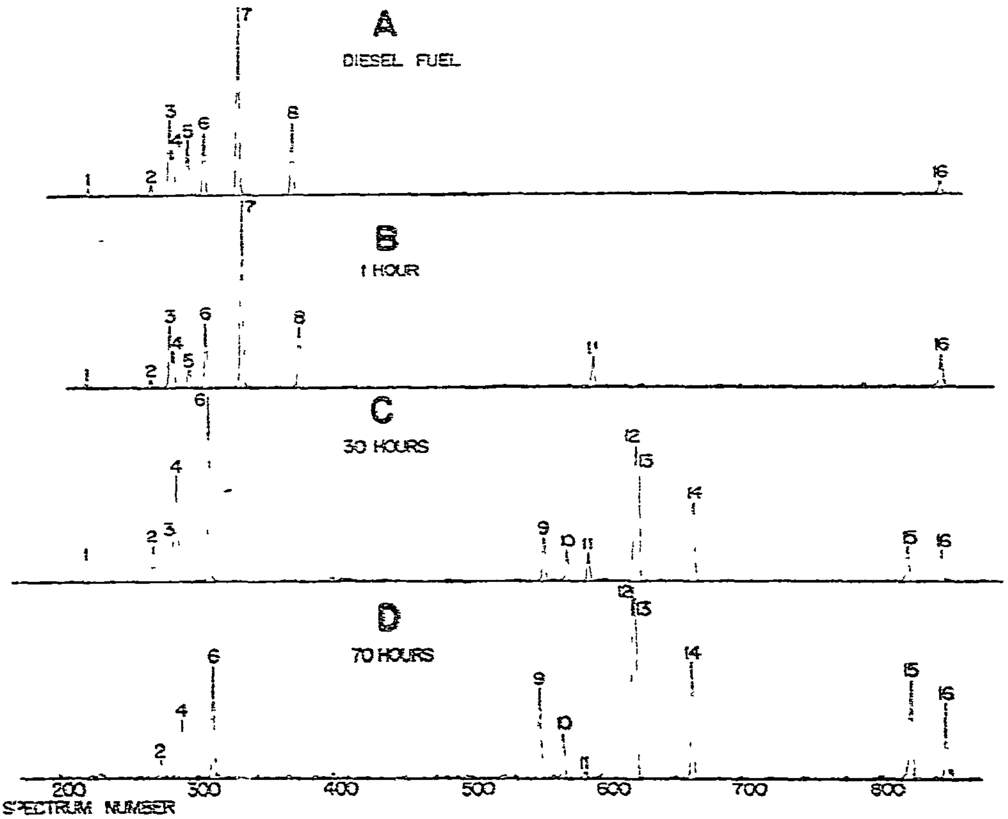

Fig. 3. Reconstructed mass chromatograms for the specific detection of C_3-benzenes and their chlorinated derivatives: MC (120 − 119) + (154 − 153) + (188 − 187). A, Diesel fuel before chlorination; B, 1 h chlorination; C, 30 h chlorination; D, 70 h chlorination. 1 = Isopropylbenzene; 2 = *n*-propylbenzene; 3 = 1-ethyl-4-methylbenzene; 4 = 1-ethyl-3-methylbenzene; 5 = mesitylene; 6 = 1-ethyl-2-methylbenzene; 7 = 1,2,4-trimethylbenzene; 8 = 1,2,3-trimethylbenzene; 9 = chloro-C_3-benzenes; 10 = chloro-C_3-benzenes; 11 = 2-chloromesitylene; 12 = chloro-C_3-benzenes; 13 = chloro-C_3-benzenes; 14 = chloro-C_3-benzenes; 15 = 2,4-dichloromesitylene; 16 = acenaphthene.

of 1 h the relative intensity of peak no. 5 (1,3,5-trimethylbenzene, mesitylene) has decreased to approximately 30% of its original value. This change can be correlated with the appearance of a chloro-C_3-benzene (peak no. 11). Peak no. 11 is then suspected to be a monochloromesitylene.

After 30 h of chlorination (trace C) the three isomeric trimethylbenzenes are no longer present, or only in trace quantities. A series of chlorinated C_3-benzenes with molecular masses of 154 (peaks 9–14) could be detected. It was not possible to determine their exact structures on the basis of their mass spectra. Peak 15 proved to be a dichloro-C_3-benzene. Only *n*-propyl-, 1-ethyl-3-methyl- and 1-ethyl-2-methylbenzenes (peaks 2, 4 and 6) remained in detectable amounts after a chlorination of 70 h. These components were obviously not oxidized; nor did they show any tendency to substitute chlorine. Peak no. 11 disappeared after 70 h reaction time, and we suspect that this chloromesitylene was chlorinated again yielding peak no. 15. Acenaphthene

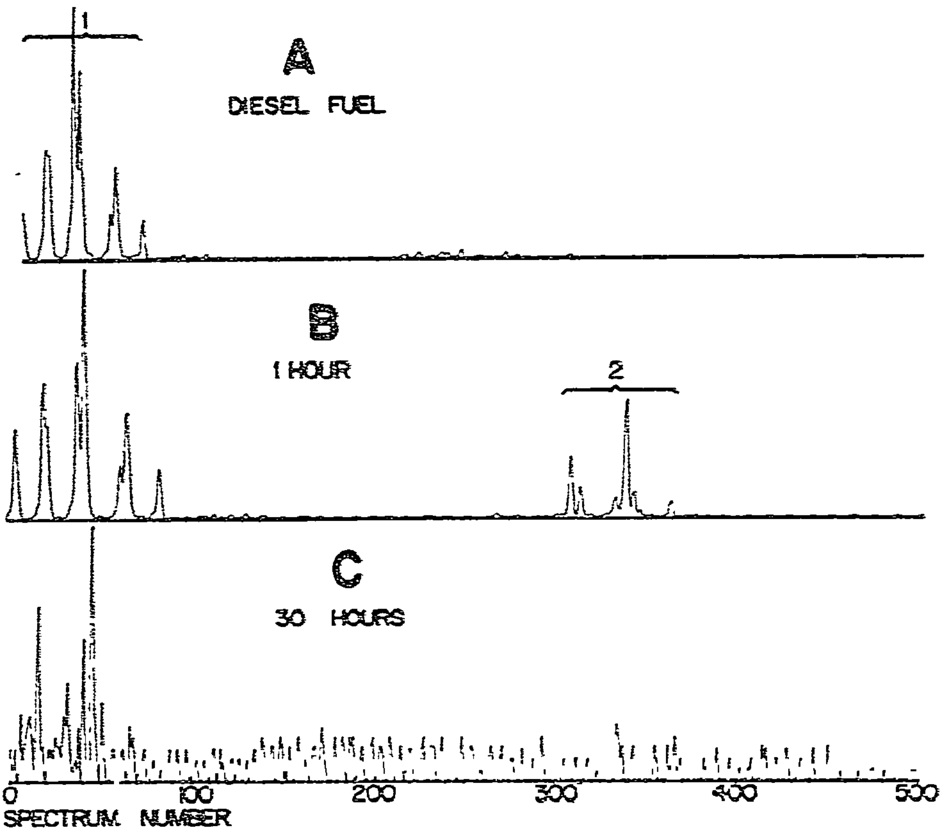

Fig. 4. Reconstructed mass chromatograms for the specific detection of C_2-naphthalenes and their chlorinated derivatives: MC(156 − 155) + (190 − 189) + (224 − 223). A, Diesel fuel without chlorination; B, 1 h chlorination; C, 30 h chlorination 1 = C_2-naphthalenes; 2 = chloro-C_2-naphthalenes.

(peak no. 16) on the other hand proved to be very stable and did not change its concentration markedly. For an exact structure elucidation of peaks no. 11 and 15, mono- and dichloromesitylenes were prepared by chlorination of an aqueous solution of mesitylene. The aromatic positions of the chlorine atoms could then be derived from their proton magnetic resonance spectra.

Some of the isomeric C_2-naphthalenes (molecular mass 156) were chlorinated after 1 h reaction time. This group of chloro-compounds is readily recognized in trace B of Fig. 4. After 30 h of chlorination (trace C) these compounds had disappeared. Since no dichloro-products could be found, we assumed that an oxidative reaction had taken place. Some C_2-naphthalenes did survive the chlorination, but their identities could not be elucidated.

Fig. 5 shows the behaviour of naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, the methylindanes and tetralene. The effect of a 30-h chlorination produced a complete elimination of the three naphthalenes. No chlorinated products could be detected. Tetralene, 1-methylindane and 2-methylindane showed the highest stability. 4-Methylindane and 5-methylindane with methyl substituents on the aro-

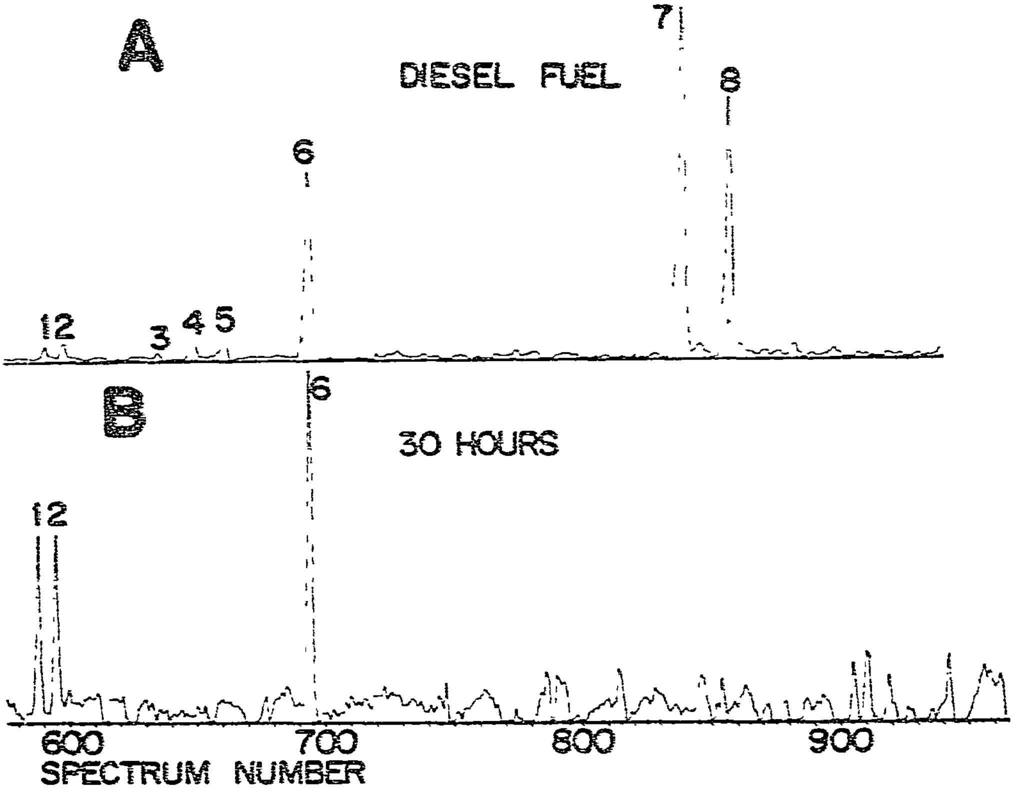

Fig. 5 Reconstructed mass chromatograms for the specific detection of naphthalene, tetralene, methylnaphthalenes and methylindanes: MC 128 + 142 + (132 − 131). A, Diesel fuel without chlorination; B, 30 h chlorination; 1 = 1-, 2-Methylindanes; 2 = 1-, 2-methylindanes: 3 = 4-, 5-methylindanes; 4 = 4-, 5-methylindanes; 5 = tetralene: 6 = naphthalene; 7 = 2-methylnaphthalene; 8 = 1-methylnaphthalene.

matic ring are degraded after the same reaction time. Phenanthrene and its methyl homologues were eliminated after 30 h of reaction, yielding no chlorinated products. Table I summarizes the results of the analyses.

In the reaction mixture a large number of interdependent reactions takes place, with the chlorination reaction competing with oxidative degradation. Because no intermediates of the oxidation were detected, we suppose the consecutive reaction steps of the oxidation to be fast. The distribution of the chlorinated products can be explained by an electrophilic aromatic substitution by chlorine. Alkyl substituents are activating and *o*/*p*-directing; if they are *m*-substituted to each other, the activating effect is enhanced.

1,3,5-Trimethylbenzene has shown the greatest chlorination rate among the C_3-benzenes, and we intend to use it as a tracer contaminant in further chlorination experiments. The fact that mainly monochlorinated products have been formed can be explained by the de-activating effect of chlorine substituents. Whether similar reactions take place under conditions present in water treatment will be further investigated.

TABLE I

AROMATIC HYDROCARBONS DETECTED IN DIESEL FUEL AND IN AQUEOUS SOLUTIONS OF DIESEL FUEL AFTER CHLORINATION

Diesel fuel

Benzenes: benzene, toluene, C_2-benzenes (*o*-, *m*-, *p*-xylol, ethylbenzene), C_3-benzenes (8 isomers), C_{4-10}-benzenes
Naphthalenes: naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, C_{2-8}-naphthalenes
Indanes: indane, C_1-indanes (4 isomers), C_{1-5}-indanes
Tetralenes: tetralene, C_{2-5}-tetralenes
Acenaphthene: biphenyl acenaphthene
Fluorenes: fluorene, C_{1-2}-fluorenes
Anthracenes: anthracene, C_{1-3}-anthracene
Phenanthrenes: phenanthrene, C_{1-3}-phenanthrenes. 4,5-methylenephenanthrene

1 h of chlorination

Chlorinated products: 2-chloromesitylene, chloro-C_{2-3}-naphthalene

30 h of chlorination

Chlorinated products: chloro-C_{2-3}-benzenes, 2,5-dichloromesitylene, chloro-C_1-indanes
Components eliminated: naphthalene, C_{1-4}-naphthalenes, C_1-indanes, phenanthrenes, anthracenes

70 h of chlorination

Components persisting after 70 h of chlorination: C_n-benzenes, chloro-C_n-benzenes, 2-chloromesitylene, dichloro-C_n-benzenes. acenaphthene

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REFERENCES

1 G. C. White, *Handbook of Chlorination*, Van Nostrand, New York, 1972.
2 R. H. Burtschell, A. A. Rosen, F M. Middleton and M. B Ettinger, *J. Amer. Water Works Ass* , 51 (1959) 205.
3 J. A. Zillich, *J. Water Pollut. Contr. Fed.*, 44 (1972) 212.
4 E. L. Barnhart and G. R. Campbell. *Water Pollution Control Series*, Environmental Protection Agency, ORM Grant No. 12020 EXG, 1972.
5 J. J. Rook, *Water Treat. Exam* , 23 (1974) 234.
6 T. A. Bellar, J. J. Lichtenberg and R. C. Kroner, *J Amer. Water Works Ass* , 66 (1974) 703.
7 K. Grob, K. Grob, Jr. and G. Grob. *J. Chromatogr* , 106 (1975) 299.
8 K. Grob and G. Grob. *J. Chromatogr.*, 90 (1974) 303.
9 W. Giger, M. Reinhard and C. Schaffner, *Vom Wasser*, 43 (1974) 343.
10 W. J. Weber, *Physicochemical Processes for Water Quality Control*, Wiley, New York, 1972, p. 378.
11 G. C. White, *Handbook of Chlorination*, Van Nostrand, New York, 1972, p 232.
12 K. Grob and G. Grob, *Chromatographia*, 5 (1972) 3.
13 N. Neuner-Jehle, F. Etzweiler and G. Zarske, *Chromatographia*, 6 (1973) 211.
14 F. Etzweiler and N. Neuner-Jehle, *Chromatographia*, 6 (1973) 503.
15 K. Grob and K. Grob, Jr., *J. Chromatogr.*, 94 (1974) 53.
16 W. H. McFadden, *Techniques of Combined Gas Chromatography/Mass Spectrometry*, Wiley, New York, 1973.